Saddle-splay modulus of a particle-laden fluid interface

S. V. Lishchuk

Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, United Kingdom

Abstract

The scaled-particle theory equation of state for the two-dimensional hard-disk fluid on a curved surface is proposed and used to determine the saddle-splay modulus of a particle-laden fluid interface. The resulting contribution to saddle-splay modulus, which is caused by thermal motion of the adsorbed particles, is comparable in magnitude with the saddle-splay modulus of a simple fluid interface.

1 Introduction

The surface free energy density of fluid interfaces depends upon their curvature. This dependence affects the nucleation in liquids [1, 2, 3], and has important role in determining the structure and dynamics of the systems with complex fluid interfaces, such as membranes or surfactants [4].

For small curvature of the interface, the dependence of the surface free energy f upon the geometry of the interface is conveniently described by the Helfrich curvature expansion [5]

$$f = \sigma + 2\kappa(H - H_0)^2 + \bar{\kappa}K \tag{1}$$

In this equation the geometry of the interface is characterized by mean curvature $H = \frac{1}{2}(1/R_1 + 1/R_2)$ and Gaussian curvature $K = 1/(R_1 R_2)$, R_1 and R_2 being principal radii of curvature of the interface. The surface tension σ, bending modulus κ, spontaneous curvature H_0, and saddle-splay modulus (or Gaussian rigidity) $\bar{\kappa}$ are the material parameters of the interface. By virtue of Gauss-Bonnet theorem, the contribution of the last term in Eq. (1) into the total free energy of the system depends on the topology of the system. Indeed, the value of the saddle-splay modulus affects the processes which involve changes in the topology of fluid interfaces [6, 7, 8, 9, 10, 11].

An interesting example of a system which can be macroscopically viewed as a complex fluid interface is the fluid interface laden with colloidal micro- or nanoparticles. To minimize total interfacial energy, particles suspended in a

bulk fluid self-assemble on the fluid interface [12]. This process, first observed by Ramsden in 1903 [13], has recently attracted significant scientific attention [14, 15, 16, 17]. It has also potential for a range of novel applications [18, 19, 20, 21, 22].

On the scale large compared to the size of the adsorbed particles, a particle-laden interface may be viewed as continuous. If the interface is isotropic on this scale, the interfacial free energy can be described by Eq. (1), and the interface can be characterized by the material parameters σ, κ, H_0, and $\bar{\kappa}$.

The present letter is devoted to the study of the saddle-splay modulus $\bar{\kappa}$ of a particle-laden fluid interface at low surface concentration of the adsorbed particles. In this case we can represent the interface as a two-dimensional fluid on a curved surface. The main contribution to the interaction between particles at low concentration comes from the excluded volume (different particles cannot occupy the same space). Hence we approximate the system by a two-dimensional hard-disk fluid on a curved surface.

Hard-disk fluids in curved geometry were used before to study packing of disks [23, 24, 25, 26], ordering phase transition [27], topological defects [28], and as a model of glass-forming liquids [24, 25, 29]. Several equations of state were proposed for hard-disk fluids in spherical [30, 31] and hyperbolic [32, 26, 33] geometries.

In the present work we shall use scaled-particle theory (SPT) [34] to derive the equation of state of two-dimensional hard-disk fluid on a curved surface. We shall then use the resulting equation of state to determine saddle-splay modulus $\bar{\kappa}$ for particle-laden fluid interface at low concentration of the adsorbed particles.

2 Saddle-splay modulus

In accordance with Eq. (1), the saddle-splay modulus is given by the derivative of the surface free energy density with respect to Gaussian curvature,

$$\bar{\kappa} = \left.\frac{\partial f}{\partial K}\right|_{K=0}. \tag{2}$$

Using the expression for the excess free energy

$$\frac{\beta F^{\mathrm{ex}}}{N} = \int_0^\rho \frac{Z-1}{\rho} d\rho, \tag{3}$$

where

$$Z \equiv \frac{\beta P}{\rho} \tag{4}$$

is the compressibility factor, $\rho = N/A$ is the number density (number of particles per unit area), P is pressure, $\beta = 1/k_B T$ is the inverse temperature, we may represent Eq. (2) in the form

$$\bar{\kappa} = \frac{\rho}{\beta} \int_0^\rho \frac{1}{\rho} \left(\frac{\partial Z}{\partial K}\right)_{K=0} d\rho, \tag{5}$$

where the derivative is taken at constant particle density ρ.

Equation (5) can be used to calculate saddle-splay modulus of the interface from the curvature dependence of the compressibility factor, which is generally given by the equation of state of the system. We shall use the SPT equation of state for a hard-disk fluid on a curved surface, which is derived in the following sections.

3 SPT equation of state for hard disks

Scaled-particle theory was originally developed by Reiss *et al* [34] and further improved afterwards [35, 36, 37, 38, 39]. Applied to the case of hard disks on a 2D plane, SPT leads to a particularly simple equation of state which is nevertheless in good agreement with computer simulation results throughout most of the fluid range of densities [40, 41].

SPT for two-dimensional hard-disk fluids in its simplest form can be summarized as follows (see textbook [42] for more details). The reversible work $W(R_0)$ is considered which is required to create a circular cavity of radius R_0 in the fluid of hard disks of radius R. The assumption is made that for $R_0 > 0$, $W(R_0)$ is given by a polynomial in R_0

$$W(R_0) = w_0 + w_1 R_0 + S(R_0)P, \quad R_0 \geq 0. \tag{6}$$

The last term $S(R_0)P$ ($S(R)$ being the area of the disk of radius R), which is dominant for large cavities ($R_0 \gg R$), follows from thermodynamics. For small cavities ($0 \leq R + R_0 \leq R$), $W(R_0)$ can be written in form

$$W(R_0) = -k_B T \ln\left[1 - \rho S(R_0 + R)\right], \ -R \leq R_0 \leq 0. \tag{7}$$

The coefficients w_0 and w_1 are then determined by requiring the work $W(R_0)$ and its derivative $W'(R_0)$, given by Eqs (6) and (7), to be continuous at $R_0 = 0$. The explicit expression for the excess chemical potential of the fluid, $\mu^{\mathrm{ex}} = W(R)$, can be determined from Eq. (6), and subsequently used to write the SPT equation of state.

In the case of the flat surface, the area of the disk is

$$S(R) = \pi R^2. \tag{8}$$

The corresponding values of the coefficients w_i are given by

$$\beta w_0 = -\ln(1 - \eta), \quad \beta w_1 = \frac{2\pi\rho R}{1 - \eta}, \tag{9}$$

where $\eta = \pi R^2 \rho$ is the hard-disk packing fraction. The chemical potential of the fluid, μ, is given by

$$\beta\mu = \ln \Lambda^2 \rho - \ln(1 - \eta) + \frac{2\eta}{1 - \eta} + \frac{\beta P \eta}{\rho}, \tag{10}$$

where Λ is de Broglie thermal wavelength. The SPT equation of state is then obtained from Eq. (10) and the thermodynamic relation

$$\frac{\partial P}{\partial \rho} = \rho \frac{\partial \mu}{\partial \rho}, \tag{11}$$

and has the form reported by Helfand *et al* [40]:

$$Z = \frac{1}{(1-\eta)^2}. \tag{12}$$

4 SPT equation of state for hard disks on a curved surface

SPT equation of state for a hard-disk fluid on a curved surface can be obtained in the same way as in the flat case described above. The difference is that expression (8) for the area of the disk of radius R is no longer valid on a curved surface. For small Gaussian curvature ($K \ll 1/R^2$) we shall replace it by the formula for the area of a geodesic disk on two-dimensional Riemannian manifold, obtained by Bertrand and Diguet in 1848 [43],

$$S(R) = \pi R^2 (1-\xi) + o(\xi), \tag{13}$$

where we have introduced the dimensionless quantity

$$\xi \equiv \frac{KR^2}{12}. \tag{14}$$

Requiring work $W(R_0)$ and its derivative $W'(R_0)$, as given by Eqs (6) and (7), to be continuous at $R_0 = 0$, we obtain the following expressions for the coefficients w_i,

$$\beta w_0 = -\ln[1 - \pi R^2 \rho (1-\xi)], \tag{15}$$

$$\beta w_1 = \frac{2\pi R \rho (1-2\xi)}{1 - \pi R^2 \rho (1-\xi)}, \tag{16}$$

and the chemical potential,

$$\begin{aligned} \beta\mu &= \ln \Lambda^2 \rho - \ln[1 - \eta(1-\xi)] \\ &+ \frac{2\eta(1-2\xi)}{1-\eta(1-\xi)} + \frac{\beta P \eta (1-\xi)}{\rho}, \end{aligned} \tag{17}$$

Equations (17) and (11) lead to the following form of the SPT equation of state for hard-disk fluid on a curved surface:

$$Z = \frac{1-\eta\xi}{[1-\eta(1-\xi)]^2}. \tag{18}$$

Figure 1 demonstrates satisfactory agreement of the compressibility factor Z calculated from Eq. (18) with the Monte Carlo results for hard disks on a sphere reported by Giarritta *et al* [27]. In the case of zero Gaussian curvature ($\xi = 0$) Eq. (18) coincides with Eq. (12).

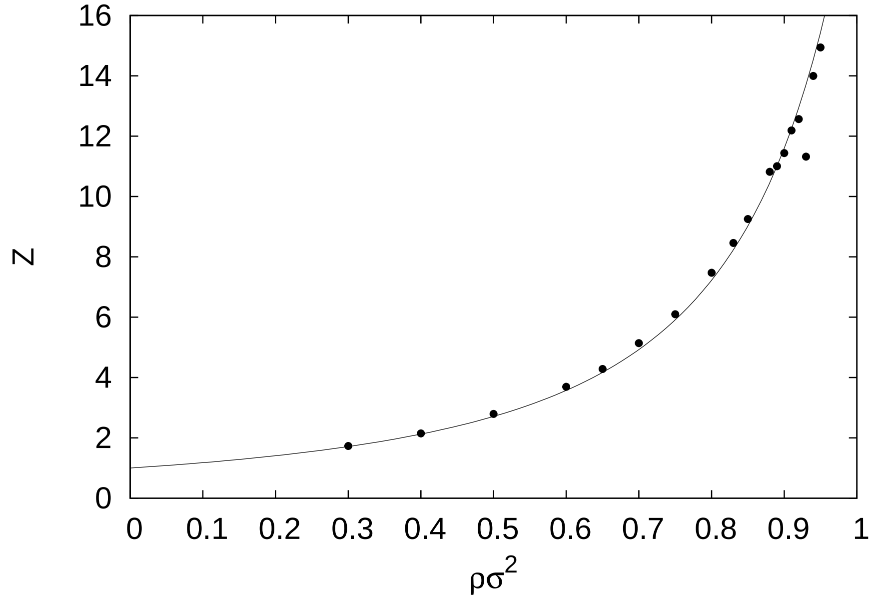

Figure 1: Compressibility factor Z as a function of reduced number density of the fluid $\rho\sigma^2$, where $\sigma \equiv 2R$ is particle diameter. Circles represent Monte Carlo results for $N = 400$ hard disks on a sphere [27], line corresponds to SPT equation of state (18).

5 Saddle-splay modulus from SPT equation of state

The expression for saddle-splay modulus is obtained by substituting the compressibility factor given by the equation of state, Eq. (18), into formula (5). The result is

$$\bar{\kappa}_{SPT} = -k_B T \frac{\eta^2(3-2\eta)}{12\pi(1-\eta)^2}. \tag{19}$$

Note that although using the truncated series in R given by the formula (13) for the area of the large disk in the expression (6) is generally not justified, it is still suitable for our purpose of calculating saddle-splay modulus since we are interested in the limit $K \to 0$.

The dependence of the saddle-splay modulus $\bar{\kappa}$ upon the disk packing fraction η, given by Eq. (19), is presented in Figure 2. The value of the saddle-splay modulus for particle-laden interfaces appears to be smaller than the values $|\bar{\kappa}| \sim 10 k_B T$ typical for lipid monolayers [44]), but is comparable to the value $|\bar{\kappa}| \approx \frac{1}{2} k_B T$ for the surfaces of simple fluids [45].

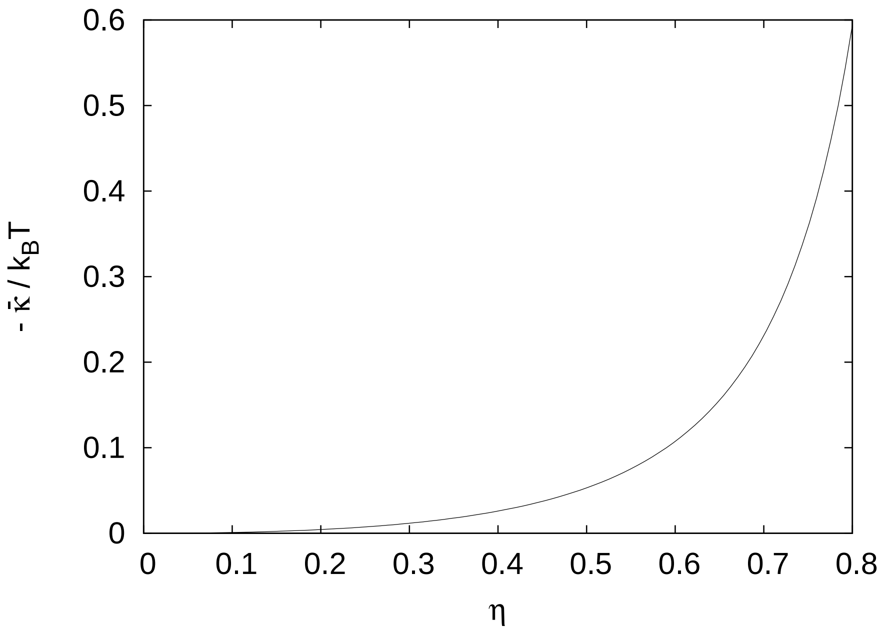

Figure 2: The dependence of the saddle-splay modulus $\bar{\kappa}$ upon disk packing fraction η, calculated using Eq. (19).

6 Conclusion

The main message of this letter is that the thermal motion of the particles adsorbed on a fluid interface contributes to the saddle-splay modulus of the interface. This result may have implications in the structure and dynamics particle-laden systems that allow topological changes, for example, fusion of particles in Pickering emulsions, or structural reorganization in particle-stabilized foams.

The simplest version of the scaled-particle theory allows construction of a rather simple equation of state for a hard-disk fluid on a curved surface. In order to improve the formula obtained for the saddle-splay modulus of a particle-laden fluid interface, it seems reasonable to attempt to construct the equation of state that gives more accurate dependence of the compressibility factor with respect to Gaussian curvature of the interface, which can be verified by using the virial expansion on the curved surface or the computer modelling of the system.

The result can also be extended by taking into account the influence on the value of saddle-splay modulus of other contributions to the interparticle interaction, such as capillary, electrostatic, van der Waals *etc*, as well as the role of particles' anisotropy. The prediction of the elastic properties of the interfaces with large concentration of particles, in which two-dimensional solid structure forms, presents another interesting and more complicated problem.

Acknowledgement

I thank Prof. C.M. Care for discussion of the results.

References

[1] R. C. Tolman. The effect of droplet size on surface tension. *J. Chem. Phys.*, 17(3):333–337, 1949.

[2] J. W. P. Schmelzer, I. Gutzow, and J. Schmelzer. Curvature-dependent surface tension and nucleation thery. *J. Col. Int. Sci.*, 178:657–665, 1996.

[3] V. G. Baidakov and G. Sh. Boltachev. Curvature dependence of the surface tension of liquid and vapor nuclei. *Phys. Rev. E*, 59(1):469–475, 1999.

[4] S. A. Safran. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes.* Addison-Wesley Publishing, 1994.

[5] W. Helfrich. Elastic properties of liquid bilayers: Theory and possible experiments. *Z. Naturforsch.*, 28c:693–703, 1973.

[6] S. A. Safran. Saddle-splay modulus and the stability of spherical microemulsions. *Phys. Rev. A*, 43(6):2903–2904, 1991.

[7] G. Gompper and D. M. Kroll. Membranes with fluctuating topology: Monte Carlo simulations. *Phys. Rev. Lett.*, 81(11):2284–2287, 1998.

[8] T. D. Le, U. Olsson, and K. Mortensen. Topological transformation of a surfactant bilayer. *Phys. A*, 276-278:379–380, 2000.

[9] H. T. Jung, S. Y. Lee, E. W. Kaler, B. Coldren, and J. A. Zasadzinski. Gaussian curvature and the equilibrium among bilayer cylinders, spheres and disks. *Proc. Natl. Acad. Sci.*, 99(24):15318–15322, 2002.

[10] D. P. Siegel and M. M. Kozlov. The Gaussian curvature elastic modulus of N-monomethylated dioleoylphosphatidylethanolamine: Relevance to membrane fusion and lipid phase behavior. *Biophys. J.*, 87:366–374, 2004.

[11] Y. Kozlovsky, A. Efrat, D. A. Siegel, and M. M. Kozlov. Stalk phase formation: Effects of dehydration and saddle splay modulus. *Biophys. J.*, 87:2508–2521, 2004.

[12] P. Pieranski. Two-dimensional interfacial colloidal crystals. *Phys. Rev. Lett.*, 45(7):569–572, 1980.

[13] W. Ramsden. Separation of solids in the surface-layers of solutions and ‘suspensions’. *Proc. R. Soc. London*, 72:156–164, 1903.

[14] B. P. Binks and T. S. Horozov. *Colloidal Particles at Liquid Interfaces.* Cambridge University Press, 2006.

[15] B. P. Binks. Particles as surfactants — similarities and differences. *Curr. Op. Coll. Int. Sci.*, 7:21–41, 2002.

[16] A. Böker, J. He, T. Emrick, and T. Russel. Self-assembly of nanoparticles at interfaces. *Soft Matter*, 3:1231–1248, 2007.

[17] A. Menner, R. Verdejo, M. Shaffer, and A. Bismarck. Particle-stabilized surfactant-free medium internal phase emulsions as templates for porous nanocomposite materials: poly-Pickering-foams. *Langmuir*, 23(5):2398–2403, 2007.

[18] A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch, and D. A. Weitz. Colloidosomes: Selectively permeable capsules composed of colloidal particles. *Science*, 298(5595):1006–1009, 2002.

[19] H. Strohm and P. Löbmann. Porous TiO_2 hollow spheres by liquid phase deposition on polystyrene latex-stabilised Pickering emulsions. *J. Mat. Chem.*, 14(17):2667–2673, 2004.

[20] B. Neirinck, J. Fransaer, O. Van der Biest, and J. Vleugels. Production of porous materials through consolidation of Pickering emulsions. *Adv. Eng. Mat.*, 9(1):57–59, 2007.

[21] B. Neirinck, T. Mattheys, A. Braem, J. Fransaer, O. van der Biest, and J. Vleugels. Porous titanium coatings bbtained by electrophoretic deposition (EPD) of Pickering emulsions and microwave sintering. *Adv. Eng. Mat.*, 10(3):246–249, 2008.

[22] L. Torres, R. Iturbe, M. J. Snowden, B. Chowdhry, and S. Leharne. Can Pickering emulsion formation aid the removal of creosote DNAPL from porous media? *Chemosphere*, 71(1):123, 2008.

[23] W. Schreiner and K. W. Kratky. Computer simulation of hard-disc packings with spherical boundary conditions. *J. Chem. Soc., Faraday Trans. 2*, 78:379–389, 1982.

[24] D. R. Nelson. Liquids and glasses in spaces of incommensurate curvature. *Phys. Rev. Lett.*, 50(13):982–985, 1983.

[25] M. Rubinstein and D. R. Nelson. Dense-packed arrays on surfaces of constant negative curvature. *Phys. Rev. B*, 28(11):6377–6386, 1983.

[26] C. D. Modes and R. D. Kamien. Geometrical frustration in two dimensions: Idealizations and realizations of a hard-disk fluid in negative curvature. *Phys. Rev. E*, 77:041125, 2008.

[27] S. P. Giarritta, M. Ferrario, and P. V. Giaquinta. Statistical geometry of hard particles on a sphere. *Phys. A*, 187(3–4):456–474, 1992.

[28] S. P. Giarritta, M. Ferrario, and P. V. Giaquinta. Statistical geometry of hard particles on a sphere—analysis of defects at high density. *Phys. A*, 201(4):649–665, 1993.

[29] F. Sausset, G. Tarjus, and P. Viot. Tuning the fragility of a glass-forming liquid by curving space. *Phys. Rev. Lett.*, 101:155701, 2008.

[30] J. Tobochnik and P. M. Chapin. Monte Carlo simulation of hard spheres near random closest packing using spherical boundary conditions. *J. Chem. Phys.*, 88(9):5824–5830, 1988.

[31] S. V. Lishchuk. Equation of state of the hard-disk fluid on a sphere from percus-yevick equation. *Phys. A*, 369:266–274, 2006.

[32] C. D. Modes and R. D. Kamien. Hard disks on the hyperbolic plane. *Phys. Rev. Lett.*, 99:235701, 2007.

[33] M. L. De Haro, A. Santos, and S. B. Yuste. Simple equation of state for hard disks on the hyperbolic plane. *J. Chem. Phys.*, 129:116101, 2008.

[34] H. Reiss, H. L. Frisch, and J. L. Lebowitz. Statistical mechanics of rigid spheres. *J. Chem. Phys.*, 31(2):369–380, 1959.

[35] R. M. Gibbons. The scaled particle theory for particles of arbitrary shape. *Mol. Phys.*, 17(1):81–86, 1969.

[36] D. M. Tully-Smith and H. Reiss. Further development of scaled particle theory of rigid sphere fluids. *J. Chem. Phys.*, 53(10):4015–4025, 1970.

[37] M. J. Mandell and H. Reiss. Scaled particle theory: Solution to the complete set of scaled particle theory conditions: Applications to surface structure and dilute mixtures. *J. Stat. Phys.*, 13(2):113–128, 1975.

[38] M. Heying and D. S. Corti. Scaled particle theory revisited: New conditions and improved predictions of the properties of the hard sphere fluid. *J. Phys. Chem. B*, 108(51):19756–19768, 2004.

[39] D. W. Siderius and D. S. Corti. On the use of multiple interpolation functions in scaled particle theory to improve the predictions of the properties of the hard-sphere fluid. *J. Chem. Phys.*, 127:144502, 2007.

[40] E. Helfand, H. L. Frisch, and J. L. Lebowitz. Theory of the two- and one-dimensional rigid sphere fluids. *J. Chem. Phys.*, 34(3):1037–1042, 1961.

[41] M. A. Cotter and F. H. Stillinger. Extension of scaled particle theory for rigid disks. *J. Chem. Phys.*, 57(8):3356–3378, 1972.

[42] J.-P. Hansen and I. R. McDonald. *Theory of Simple Liquids*. Academic Press, Amsterdam, 2007.

[43] M. J. Bertrand and M. Diguet. Demonstration d'une théorème de M. Gauss. *J. Math. Pur. Appl.*, 13:80–86, 1848.

[44] D. Marsh. Elastic curvature constants of lipid monolayers and bilayers. *Chem. Phys. Lipids*, 144:146–159, 2006.

[45] A. E. van Giessen and E. M. Blokhius. Determination of curvature corrections to the surface tension of a liquid–vapor interface through molecular dynamics simulations. *J. Chem. Phys.*, 116(1):302–310, 1002.